Impact of anthropogenic pollution on the soil near the industrial area of Hrazdan town

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Abstract. Identifying the distribution of a number of heavy metals near the industrial area, taking into account the wind rose in the region during the period of operation of the Hrazdan Thermal Power Station and the Hrazdan Cement Plant was investigated in a radius of one km. In a series of experiments, was found a decreased concentration of arsenic and mercury in soil samples by an average of 27% with distance from the industrial area. In that direction, in the soil sample, there is an increase in the concentration of zinc and nickel by an average of 25.5%, as well as an increase in the concentration of copper by 19%. At the same time along the sampling line, the comparative series generally has the following sequence: As<Ni<Co<Cu<Zn<Pb. In the quantitative assessment of soil, contamination was compared to geo-ecological coefficients: the danger level of soil contamination and the total pollution index. Their calculation was based on the values of heavy metals concentration according to Clark and their maximum allowable concentration. Our forthcoming studies will focus on identifying the dose-effect-rose-wind relationship in arable soils with varying degrees of metal contamination as a result of long-term anthropogenic pollution.

1 Introduction

The development of industry is inextricably linked to the increasing technogenic load on the environment, where the main sources of pollution are various industrial enterprises, motor transport, energy complexes, etc [1]. The main pollutants are heavy metals (HMs) and their stable compounds, which have an irreversible impact on the quality of the natural environment [2]. In this context, the state of the ecosystem as a whole and the state of its individual components is significantly affected not only by the pollution itself but also by the distribution of pollutants by natural phenomena, such as the wind rose [3]. Certainly, almost all HMs are required by living organisms. But spreading through the air streams, they get to the ground cover, to the water surface, whereas as a result of migration they accumulate and enter the trophic chain in various components of the biota [4,5]. The danger of increased content of HMs in the ecosystem is due to the fact that most chemical elements

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have high biological activity and can cause toxic effects on organisms in small quantities [6]. That is why identifying the mechanisms and patterns of behaviour and distribution of heavy metals in the environment is of particular interest as well as of great practical importance.

Hrazdan town is one of the most important industrial and energy centres in the Republic of Armenia. The Hrazdan Thermal Power Station (HTPS) and Hrazdan Cement Plant (HCP) are located here as well as other important enterprises. Due to the high spatial mobility of polluted air caused by the wind rose in the region, air basin control is an urgent environmental protection issue in industrial areas [7].

Soil is the main medium into which HMs and metalloids enter, including from the atmosphere and aquatic environment. Pollutants arriving in the air get into the soil, where they accumulate as a result of migration and enter various components of the biota [8]. Such natural reservoirs can "reflect" not only in situ pollution processes, but also those that took place long ago [9]. Therefore, a qualitative analysis of soils with respect to the degree of contamination is crucial for solving the problem of the ecological state of the region [10]. In our research the soil cover is represented mainly by chestnut soils and chernozem. The loss of the upper fertile layer is characteristic of such soils under industrial pollution [11]. The peculiarities of the wind rose direction in the area were especially taken into account.

The aim of our research was to study the harmful effects of the migration of some heavy metals (Pb, Zn, Cu, Co, Ni) and metalloid (As), taking into account the wind rose in the region, on the environment during the operation of a thermal power station and a cement plant in the industrial zone of the Hrazdan town.

2 Materials and methods

The objects of the study were some heavy metals and metalloids both of first hazard class (mercury (Pb), arsenic (As), zinc (Zn)), and second hazard class (copper (Cu), cobalt (Co), nickel (Ni)) [12]. The study area covered a significant part of the Hrazdan industrial district in the south-western direction (HTPS and HCP), taking into account anthropogenic load and the dominating in this way of the regional wind rose [13].

Soil samples under dry-weather conditions were taken from a depth of up to 20 cm at control points using the envelope method. Point sampling was performed by using non-metallic tools. A combined soil sample was prepared by mixing at least five incremental samples taken from the same site. Afterward, the samples were placed in dark glass containers and transported at +4°C for laboratory (instrumental) measurements for 24 hours [8]. Soil samples were examined under direct exposure to X-rays using a Termo Scientific™Niton™ XRF Portable Analyser. Each sample was examined at least 3 times and the results were averaged according to the arithmetic mean law. The instrument data (mg/kg) were considered as the final result for the soils. Studies were performed on 10 soil samples, the results of which are presented in units/mg/kg, respectively [14]. All the experimental data had up to 5 technical replicates and were statistically processed [15].

3 Results and discussion

Contamination by HMs and metalloids is associated with their widespread use in industrial production. Today, they are the second most hazardous substances (the second ones only to pesticides) but far ahead of carbon dioxide and sulfur dioxide, which, obviously, may become more hazardous than nuclear power plant waste and solid waste in the near future [16]. Cement production has an impact on the environment at all stages of the production process [17]. It has been shown that the highest percentage reduction in HMs content with distance from the source has been recorded for Pb, slightly less for Zn and Cu, averaging 52% [18]. On the other hand, a significant impact on various components of the natural environment in the form of the accumulation of heavy metals is contributed by thermal power plants [19].

Recently, we have started a series of experiments to determine the impact of the anthropogenic load of a number of industrial enterprises in Armenia, which is expressed in quantitative and qualitative changes in the content of HMs and metalloids in samples near arable soils. Investigations have been carried out to assess the degree of soil near operating (Kajaran Copper-Molybdenum Plant and Hrazdan Cement Plant) and currently not operating (Alaverdi Mining and Metallurgical Plant and Vanadzor Chemical Plant) industrial enterprises [15]. According to the results, the highest values of the content of the studied HMs in the anthropogenic HCP zone were recorded in the range of 0.5-2.5 km as the following comparative series: Zn> Pb > Cu. At a distance of 25 km from the enterprise, the average concentration of Zn and Pb decreased by 78%, Cu - by 53%. The comparative range for the tested pollutants is as follows: Zn > Cu> Pb > Co> Mo. The research was continued in this direction for distances of up to one km. According to the information on the wind rose map in Hrazdan town, the prevailing wind direction is southwest (31%) [20]. The area of pollutant dispersion coming into the atmosphere of the industrial area will prevail precisely in this direction, where the private arable soils of the region are located. At the same time, the maximum emission of pollutants from the HTPS is observed in the winter (heating) season, when the wind speeds are low. In the case of HCP, the situation is reversed, since the construction period falls during the spring-summer period when wind speeds increase, contributing to a more intensive dispersion of pollutants. At the first stage of our experiments, the concentration changes in some of HMs and metalloid were determined in soil samples with distance from pollution sources (Table 1). The results obtained were not unambiguous.

Table 1. Concentration changes in a number of heavy metals and metalloid at a distance from the pollution source near of the Hrazdan industrial area.

Distance from the source of pollution, km	The concentration of heavy metals and metalloid in soil samples, mg/kg					
	As	Pb	Zn	Cu	Ni	Co
1.0	40.7±0.34	126.4±4.32	115.6±3.21	92.8±1.59	71.4±0.86	84.0±0.85
0.8	45.0±0.14	168.6±2.45	89.0±1.97	72.6±1.12	72.4±0.76	trace
0.6	50.5±0.32	165.4±5.62	98.5±2.45	87.3±1.25	57.7±0.43	trace
0.4	53.1±0.29	166.0±5.49	101.9±2.67	79.9±0.95	70.1±0.65	trace
0.2	55.3±0.34	175.8±6.91	83.7±1.83	75.2±1.04	56.9±0.39	trace

Thus, the concentrations of As and Pb decreased on average by 27% with distance from the industrial area. In quantitative meaning, the concentration of lead was three times higher than the concentration of arsenic along the sampling line. In the case of other elements, the opposite pattern is observed, which indicates the following. As we move away from the source of pollution, soil samples show a concentration increase of zinc and nickel of an average of 25.5%, and also a 19% increase in the concentration of copper. Cobalt is also of particular interest. Its traces were found in soil samples near the pollution source, and already along the sampling line at a distance of one km, its concentration in soil samples was 84.0±0.85 mg/kg. Based on the results obtained, it can be assumed which elements are subject to air migration caused by the action of the wind rose in this region. To interpret the results given, some geoecological coefficients such as soil contamination hazard level (K_0) and total pollution index (Z_c) were compared taking into account Clarke concentration (CC) and maximum permissible concentration (MPC) of chemical elements by [22,23] (Table 2).

Table 2. The value of some geoecological coefficients in soil samples near of the Hrazdan industrial area.

Distance from the source of pollution, km	**Soil contamination hazard level (*K*₀)***						**Total pollution index (Z_c)****
	As	**Pb**	**Zn**	**Cu**	**Ni**	**Co**	
1.0	4.07±0.76	3.95 ± 0.74	1.16 ± 0.09	1.69 ± 0.19	10.66±0.43	3.36±0.37	16.29
0.8	4.54±0.38	5.27 ± 0.35	0.89± 0.05	1.32 ± 0.09	10.81±0.36	-	17.09
0.6	5.05±0.63	5.17 ± 0.86	0.98± 0.02	1.59 ± 0.11	8.61±0.21	-	17.95
0.4	5.31±0.58	5.19 ± 0.91	1.02± 0.07	1.45 ± 0.13	10.46±0.51	-	18.58
0.2	5.53±0.55	5.49 ± 0.81	0.84± 0.06	1.37 ± 0.08	8.49±0.19	-	18.96

Note:*The value of $K_0 > 1$ pollution level was high danger; ** the summary pollution level was classified as low with $Z_c < 16$ contamination is considered as non-dangerous; with $16 < Z_c < 32$ contamination is moderately dangerous; with $32 < Z_c < 128$ contamination is dangerous; with $Z_c > 128$ contamination is extremely dangerous [23]

When the value of the coefficient is $K_0 > 1$, then the risk of pollution is high, and it may have exorbitant values, especially near the source of pollution. The risk of contamination increases in direct proportion to the content of HMs in the studied samples, taking into account their MPC [24]. It was established that soil samples taken at the studied sites at a distance of 0.2 km from the pollution source had a moderately dangerous level of contamination. With the subsequent removal from the enterprises, the value of the total pollution index (Z_c) decreased by 16%.

4 Conclusions

The accumulation and migration of HMs affect their entry into living organisms through the food chain "natural breed (clark)-soil-plant-animal-human", bringing to the forefront research in environmental protection for environmental and health management. In the course of this research, the findings obtained and the comparative analysis of soil samples from the industrial area of Hrazdan town showed that the top soil layer of sites located up to 0.2 km away from the sources is contaminated with lead and arsenic. As we move away from the sources up to one km, there is a significant increase in the concentrations of other elements (Ni, Co, Cu, and Zn). The comparative line up to one km as a whole is presented in the following sequence: As<Ni<Co<Cu<Zn<Pb. Assessment of the degree of anthropogenic load of environmental pollution of the territories will be an informative parameter in case based on the meanings of geoecological coefficients. Probably, the processes of HMs migration in anthropogenic polluted territories may be due to the dominance of the south-western direction of the wind rose in this region. Taking into account the dominant wind directions, there is a significant increase in the anthropogenic load on the soil by Ni, Co, Cu, and Zn.

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